

Evaluation of Portable X-ray Fluorescence for Gypsum Quantification in Soils

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Abstract: The use of field portable X-ray fluorescence (XRF) spectrometry as a quantification tool for gypsum content in soils of West Texas and southern New Mexico, USA, was evaluated. Six sites were evaluated with gypsum contents ranging from less than 10% to greater than 90%. Samples collected from each site were scanned in the field using XRF and then transported to the laboratory for additional XRF scanning. Variables that might affect XRF scanning results, such as scanning time, particle size, moisture content, and so on, were evaluated. Both gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and calcite (CaCO_3) were quantified using standard laboratory techniques. Three data sets were compared: (1) soil characterization data, obtained from the National Soil Survey Laboratory Research Database in Lincoln, NE; (2) quantitative X-ray diffraction; and (3) portable XRF (PXRF). The best correlation of gypsum XRF data (via Ca quantification minus calcite content) and laboratory data was between PXRF and quantitative X-ray diffraction ($R = 0.96$). On average, PXRF provided results within 6% of soil characterization data, the current laboratory standard for gypsum quantification. Field PXRF shows considerable promise as a rapid, quantifiable measure of gypsum in soils.

Key words: XRF, gypsum, aridisols.

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Soils containing a significant amount of gypsum are common in the southwestern United States and in selected arid regions of the world. They are in arid and semiarid environments where salts accumulate because of high evapotranspiration. Gypsic horizons are defined by the Soil Survey Staff (1999) as horizons “more than 15 cm thick... noncemented... with 5% or more (by weight) gypsum and 1% or more (by weight) secondary visible gypsum.” Most soils with gypsic horizons are grouped in the suborder “Gypsisols” in soil taxonomy (Soil Survey Staff, 1999). Gypsid soils account for 14,061 km² in the southwest United States (Texas, New Mexico, Arizona, California, Utah, and Nevada). The World Reference Base system of soil taxonomy refers to gypsum-rich soils as “Gypsisols” and estimates their extent to be 100 million ha worldwide (International Union of Soil Science, 2006). They occur in the Near East and adjacent Central Asian republics, the Libyan and Namib deserts in Africa, and in southeast and central Australia (International Union of Soil Science, 2006). Gypsic soils pose a threat to buildings and

infrastructure via irregular subsidence, caving of trenched walls, and corrosion of both iron and concrete.

At present, gypsum quantification for classification is based on precipitation with acetone and associated electrical conductivity readings (Soil Survey Staff, 2004) or an increase in soluble calcium and magnesium content upon dilution (US Salinity Laboratory Staff, 1954); with both methods requiring extensive laboratory work. Furthermore, the methods are prone to interferences such as incomplete dissolution of gypsum and simultaneous precipitation of Na and K sulfates with gypsum (Soil Survey Staff, 2004).

Another reason for quantifying gypsum in soils is its interference with grain size analyses, one of the most fundamental laboratory procedures run on soil samples. The pipette method (Soil Survey Staff, 2004) and hydrometer method (Gee and Bauder, 1986) are commonly used to determine the percentage of sand, silt, and clay based on particle settling rates in aqueous suspensions. With soils containing appreciable gypsum, grain size analyses are usually erroneous because of (i) the solubility of gypsum itself (it dissolves in water during the analysis) and (ii) it causes flocculation of the suspension, which leads to abnormally high sedimentation rates, producing meaningless results.

In recent years, X-ray fluorescence (XRF) analysis has been widely used to quantify elements in soil, geological, and environmental studies. The mineralogy of selected soils in Puerto Rico was evaluated in a study by Jones et al. (1982). They used a combination of X-ray diffraction (XRD), electron microscopy, and XRF techniques to describe the mineralogical composition of highly weathered soils. Busacca and Singer (1989) used XRF to quantify a range of elements (Na, Mg, Al, Si, K, Ca, Ti, Fe, Zr, Mn, Cr, Ni, Cu, Zn, Rb, Sr, and Nb) in the silt fractions of soils in the Sacramento Valley of California. Results were element specific, but ranged from very low concentrations (<250 ppm for Zr) to very high concentrations (>50% SiO_2). Kalnicky and Singhvi (2001) evaluated the detection limits, scanning times, and standardization of portable XRF (PXRF) specifically as they relate to metal contamination of sediments and soils. They scanned samples at 15, 30, 60, 120, 240, and 480 sec, evaluating 23 different elements. They concluded that the method detection limit generally decreases with increased analysis time and that elements at high concentrations tended to have higher detection limits than those at lower concentrations. As such, they proposed that PXRF provides a viable, cost-effective approach for on-site analysis. Celis (1996) used high-voltage XRF (145 kV) to quantify Au in ores down to 0.5 ppm. Schulin et al. (2007) used XRF to evaluate heavy-metal concentrations in agricultural soils in Bulgaria. They analyzed 19 elements including Ca and found higher concentrations of Pb, Cd, Zn, Cu, and As in Fluvisols than Chromic Luvisols. The former averaged 121, 2.0, 275, 61, and 132 mg kg⁻¹, and the latter averaged 50, 0.34, 104, 36 and 31 mg kg⁻¹, respectively. Ge et al. (2005) have discussed the application of PXRF for *in situ* mineral exploration in China in the 1980s and 1990s. Their extensive work included evaluation

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of surface geometry, mineral heterogeneity, the influence of moisture, and the influence of grain size on XRF readings. Weindorf et al. (2008) concluded that PXRF proved to be useful for field evaluation of metals, such as As, Cu, and Zn, by providing detection limits averaging 12, 33, and 18 mg kg⁻¹, respectively, in organic materials. Furthermore, they proposed that PXRF may be preferable to ICP-AES analysis for quantifying high levels of Ca because the former easily handles high elemental concentrations (>10,000 mg kg⁻¹) with direct readings, whereas the latter requires dilutions for accurate quantification. As a precursor to this present study, Zhu and Weindorf (2009) evaluated the ability of PXRF to accurately quantify Ca on various natural and artificially constructed soils in the laboratory. They concluded that PXRF can detect and quantify total soil Ca rapidly, accurately, and consistently.

The use of PXRF allows researchers to quantify, *in situ*, a range of elements in soils in a matter of seconds. Several manufacturers produce such equipment; among them are Thermo Scientific (Boston, MA), Bruker AXS (Madison, WI), and Innov-X Systems (Woburn, MA). Thus, if PXRF can provide precise gypsum quantification in the field, great savings in laboratory time could result. The goal of this study was to compare the use of PXRF for gypsum quantification with XRD and acetone precipitation laboratory methods.

MATERIALS AND METHODS

Field Sampling

Fieldwork was conducted during May 2008, in Culberson and Presidio Counties, Texas, and Otero County, New Mexico (Fig. 1). Sites were selected to evaluate gypsum contents in soils

of less than 10 wt % to greater than 90 wt %. Sites 1 and 2 were hand excavated to a depth of approximately 40 cm; backhoe pits of greater than 1 m were used to collect samples from sites 3 to 5. Sampling site locations are given in Table 1. Profiles were described in the field. Samples were collected from each horizon, sealed in plastic bags, scanned in triplicate, and transported to the laboratory for quantitative XRD (QXRD) analysis.

The soil at site 1 was an unnamed series (*Leptic Haplogypsid*). Slopes range from 0% to 5%. Mean annual precipitation is about 13 inches (330 mm), and mean annual temperature is about 63 °F (17 °C). The Chngas series (*Ustic Haplogypsid*) (site 2) consisted of thin gravelly alluvium over lacustrine sediments from the Presidio Bolson, which is estimated to be approximately 500,000 years old. Slopes range from 0% to 5%. Mean annual precipitation is about 11 inches (279 mm), and mean annual temperature is about 69 °F (21 °C). The Talos series (*Calcic Argigypsid*) (site 3) consisted of very deep, well-drained, slowly permeable soils formed in clayey gypsiferous alluvium. These nearly level soils are on basin floors. Slope range from 0% to 3%. Mean annual precipitation is about 11 inches (279 mm), and the mean annual temperature is about 63 °F (17 °C). The Peligro series (*Leptic Haplogypsid*) (site 4) consisted of very deep, well-drained, moderately permeable soils formed in eolian gypsiferous sediments. These nearly level to strongly sloping soils are on lunettes or parna dunes on basin floors. Slope range from 1% to 15%. Mean annual precipitation is about 11 inches (279 mm), and the mean annual temperature is about 63 °F (17 °C). The Flake series (*Calcic Argigypsid*) (site 5) consisted of very deep, well-drained, moderately permeable soils formed in fine loamy alluvium. These nearly level soils are on basin floors or rise basins. Slope range from 1%

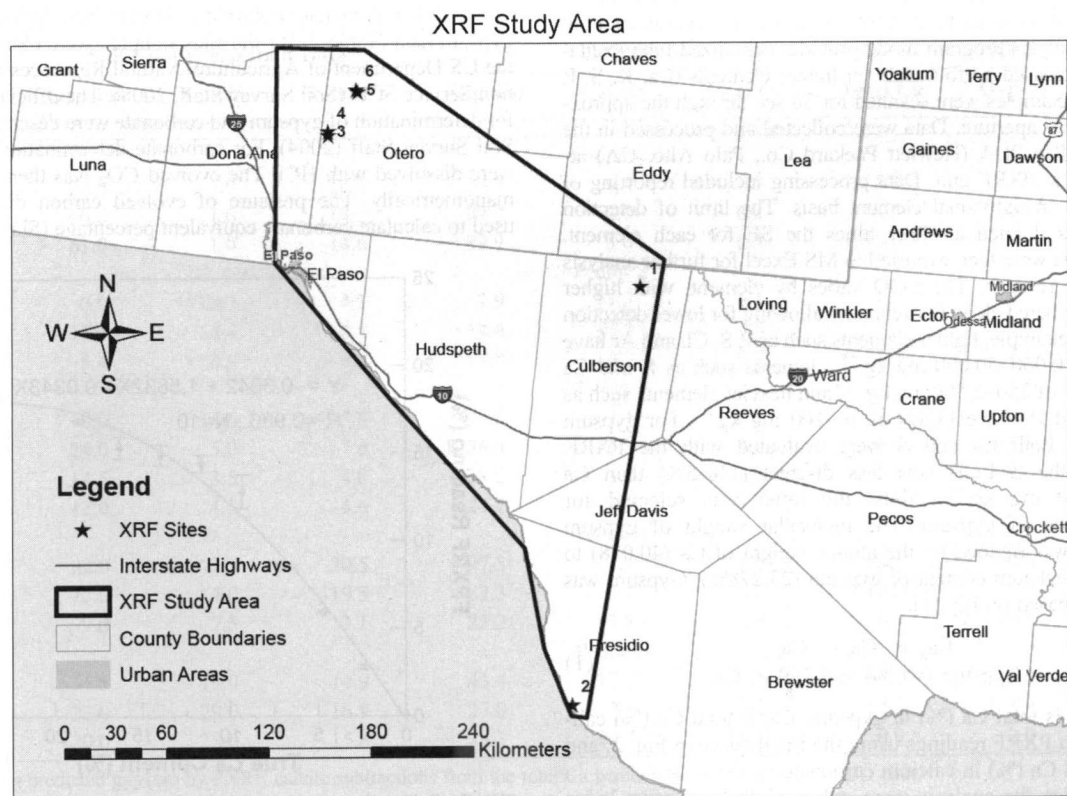


FIG. 1. Location of XRF study in West Texas and southern New Mexico, USA.

TABLE 1. Location of Sampling Sites in Texas and New Mexico, USA

Site	Latitude (°N)	Longitude (°W)	Altitude (m)	Land Use
1	31.88297	-104.32691	1059	Private land
2	29.66969	-104.48153	822	Public land
3	32.49197	-106.33369	1211	White sands missile range
4	32.51402	-106.33604	1213	White sands missile range
5	32.73656	-106.18625	1210	White sands missile range

to 15%. Mean annual precipitation is about 9 inches (229 mm), and the mean annual temperature is about 61 °F (16 °C). Soil series names at sites 1 and 2 are provisional; sites 3 to 5 are established soil series names.

Portable X-ray Fluorescence Analysis of Ca Abundance

A battery operated, Innov-X Systems Alpha series PXRF (tantalum X-ray tube operated at 35 kV) (Innov-X Systems, Woburn, MA) was used in this study. A stainless steel 316 standardization clip was used to standardize the instrument. The alloy contained 16.130% Cr, 1.780% Mn, 68.760% Fe, 10.420% Ni, 0.200% Cu, and 2.100% Mo and was fitted tightly over the aperture. The instrument was operated with the light element analysis program mode engaged using a proprietary standard configuration known as *soil mode*. Soil mode uses a scatter normalization algorithm (per EPA Method 6200) for soil, liquids, and powders, allowing for sequential analysis of atomic numbers $Z = 15$ (phosphorus) to $Z = 92$ (uranium). Utilization of light element analysis program mode provides optimized tube excitation for increased performance on lighter elements (Ca, K, S, P, Cl, and I). Samples were scanned for 30 sec through the approximately 2-cm aperture. Data were collected and processed in the on-board iPac PDA (Hewlett Packard Co., Palo Alto, CA) attached to the PXRF unit. Data processing included reporting of the SE on an individual element basis. The limit of detection (LOD) was defined as three times the SE for each element. Logged data were then exported to MS Excel for further analysis such as correlation. The LOD varies by element, with higher atomic numbered elements generally allowing for lower detection limits. For example, lighter elements such as P, S, Cl, and Ar have LODs of 10,000–50,000 mg kg⁻¹, elements such as K and Ca have LODs of 250–2,500 mg kg⁻¹, and heavier elements such as Fe, Cu, and Zn have LODs of 10–100 mg kg⁻¹. For gypsum evaluation, both Ca and S were evaluated with the PXRF. However, the S LOD was less discreet (1%–5%) than Ca (250–2,500 mg kg⁻¹); thus, the latter was selected for quantification of gypsum. The molecular weight of gypsum (172.171) was divided by the atomic weight of Ca (40.078) to obtain the calcium content of gypsum (23.278%). Gypsum was quantified based on Eq. (1).

$$\text{Gypsum (wt \%)} = 4.299 \times \text{Ca}_g \quad (1)$$

where Ca_g is total Ca (%) in gypsum, Ca_t is total Ca (%) calibrated from PXRF readings using the fitted curve in Fig. 2, and Ca_c is total Ca (%) in calcium carbonate.

Samples for analysis were collected from gypsum-laden soil horizons at sites 1 to 5 and sealed in approximately 1-L

plastic bags. The samples were lightly crushed and mixed inside the bag using hand pressure. Fine, disaggregated, mixed material easily fell to the bottom of the bags. The bags were then inverted to provide a smooth, continuous surface on which the aperture could be placed and scanned in triplicate for 30 sec each.

Laboratory Calibration of PXRF

Calibration of the PXRF was accomplished using 10 mixtures of reagent grade gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with washed quartz sand (Table 2). The mixtures were made on a gravimetric basis as follows: 100% gypsum, 0% sand; 90% gypsum, 10% sand; 80% gypsum, 20% sand; and so on. The bagged mixtures were scanned in triplicate for 30 sec each and averaged to obtain scanned Ca content. Calcium content of the mixtures was calculated with Eq. (1).

Using a polynomial fit to regress the data sets, an R^2 of 0.986 was achieved (Fig. 2). The bars in Fig. 2 are SE within the triplicates. Evaluation of PXRF calibration data shows that, at low levels of gypsum, PXRF tends to overestimate total Ca, whereas at extremely high levels of gypsum (>80%), the PXRF underestimates total Ca.

Moisture and particle size were considered as possible variables influencing results. Samples were scanned for 30 sec each under (i) field moist conditions, (ii) after oven drying at 40 °C for 48 h, and (iii) after grinding to pass a 2-mm sieve. Preliminary results showed no significant differences ($P < 0.05$) between these treatments in 14 of 16 samples; thus, field moist PXRF scan data were used for comparison to QXRD and soil characterization data (SCD). Statistical comparisons notwithstanding, fine grinding (<500 μm) may produce better results from PXRF if gypsum exists as larger crystals rather than being finely disseminated.

Soil Characterization Database

Calcium carbonate (referred to as carbonate equivalent) and gypsum data (Table 2) for the sites sampled were obtained from the US Department of Agriculture–Natural Resources Conservation Service SCD (Soil Survey Staff, 2008). The official methods for determination of gypsum and carbonate were described by the Soil Survey Staff (2004). For carbonate determination, samples were dissolved with HCl. The evolved CO_2 was then measured manometrically. The pressure of evolved carbon dioxide was used to calculate carbonate equivalent percentage (Sherrod et al.,

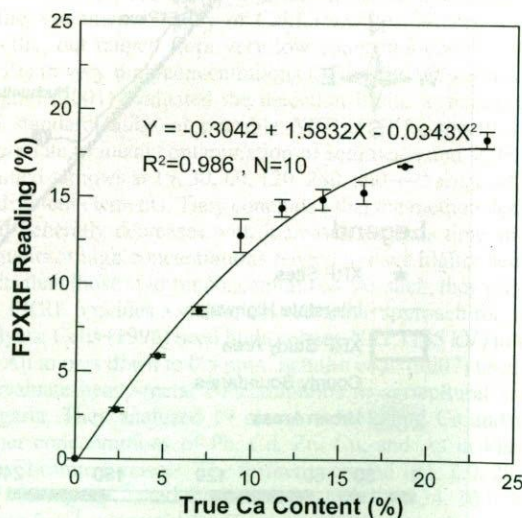


FIG. 2. Calibration curve created by regressing true Ca percentage against PXRF Ca percentage.

TABLE 2. Calibration Mixtures and PXRF Readings for Ca Percentage

ID	Gypsum	Sand	Ca Std.	Reading 1	Reading 2	Reading 3	Average
				%			
1	0	100	0	0	0	0	0
2	10	90	2.328	5.340	7.609	5.176	6.042
3	20	80	4.656	12.161	11.407	8.457	10.675
4	30	70	6.983	12.923	11.078	11.715	11.905
5	40	60	9.311	14.274	9.411	15.796	13.160
6	50	50	11.639	15.997	15.748	16.346	16.030
7	60	40	13.967	15.315	14.308	13.818	14.481
8	70	30	16.300	15.667	16.143	15.295	15.702
9	80	20	18.622	18.390	16.902	17.458	17.583
10	100	0	23.278	19.880	19.129	18.730	19.246

2002). Such a technique is field portable and consistent with laboratory determinations. Gypsum quantification was accomplished with acetone precipitation. Soil samples were mixed with water to dissolve the gypsum. Acetone was then added to a portion of the clear extract to precipitate the dissolved gypsum. After centrifuging, the gypsum was redissolved in water. The electrical conductivity of the solution was measured. Gypsum is reported in meq 100 g⁻¹. This method is not field portable, thus limiting its use by soil surveyors in the field.

Quantitative X-ray Diffraction

Quantitative XRD analysis was used to provide an estimate of calcite and gypsum weight percentages for comparison to

PXRF. Subsamples from previously PXRF-scanned samples were ground to pass a 2-mm sieve, then scanned as pressed powders on a Siemens D5000 X-ray diffractometer (New York, NY) (40 kV, 30 mA) at 0.02° 2 θ steps, with 2 sec per step, from 2°–70° 2 θ . Zincite (ZnO) was used as an internal standard. Quantitative interpretations of XRD data were made using RockJock software (Eberl, 2003).

Both QXRD and SCD data are reported as percent calcite and percent gypsum on a weight basis. Two types of comparison to PXRF were undertaken: (i) QXRD and SCD carbonate and gypsum percentages were converted to total calcium and compared with PXRF total calcium and (ii) PXRF total calcium was converted to gypsum after correcting for carbonate-calcium

TABLE 3. Gypsum, Calcite, and Calcium Weight Percentages From the SCD, QXRD, and PXRF for Five Soil Pedons in West Texas and Southern New Mexico, USA

Depth cm	Soil Characterization Data			QXRD			PXRF		
	Gypsum	Calcite	Total Ca	Gypsum	Calcite	Total Ca	Total Ca	Gyp-a [†]	Gyp-b [‡]
					%				
					Pedon 1				
0–4	55.0	3.0	14.0	26.2	6.4	7.1	5.8	19.6	13.8
4–10	60.0	1.0	14.3	89.2	2.0	6.2	14.5	60.4	58.6
10–30	61.0	1.0	14.6	89.9	3.0	6.5	15.8	66.1	62.7
					Pedon 2				
0–6	0.0	10.3	4.1	7.9	17.3	5.7	4.2	0.3	0.0
6–20	13.5	8.4	6.5	14.8	16.7	6.5	5.5	9.0	0.0
20–30+	5.4	8.9	4.8	14.9	16.1	5.7	4.5	4.1	0.0
					Pedon 3				
18–36	0.0	14.5	5.8	8.2	17.1	6.3	4.1	0.0	0.0
53–81	24.0	5.0	7.6	26.6	6.3	4.5	6.9	21.1	18.9
81–130	14.5	3.5	4.8	38.2	3.8	2.8	10.5	39.0	38.5
130–150	12.0	4.5	4.6	24.7	3.9	2.7	5.6	16.4	17.4
					Pedon 4				
3–20	82.0	3.5	20.5	97.5	1.9	8.6	15.5	60.6	63.4
58–89	77.0	4.0	19.5	82.3	3.4	8.6	15.0	57.7	58.7
157–176	9.0	2.5	3.1	22.2	2.8	1.9	4.9	16.8	16.2
					Pedon 5				
25–48	31.5	19.0	14.9	43.4	17.9	10.1	11.9	18.5	20.4
71–102	23.0	29.0	16.9	27.0	27.8	13.2	12.5	3.9	6.0
102–160	20.0	28.0	15.8	39.3	20.7	11.1	10.9	0.0	11.4

[†]Gyp-a = predicted gypsum by PXRF, calcite subtractions from the total Ca percentage were made with SCD data.

[‡]Gyp-b = predicted gypsum by PXRF, calcite subtractions from the total Ca percentage were made with QXRD data.

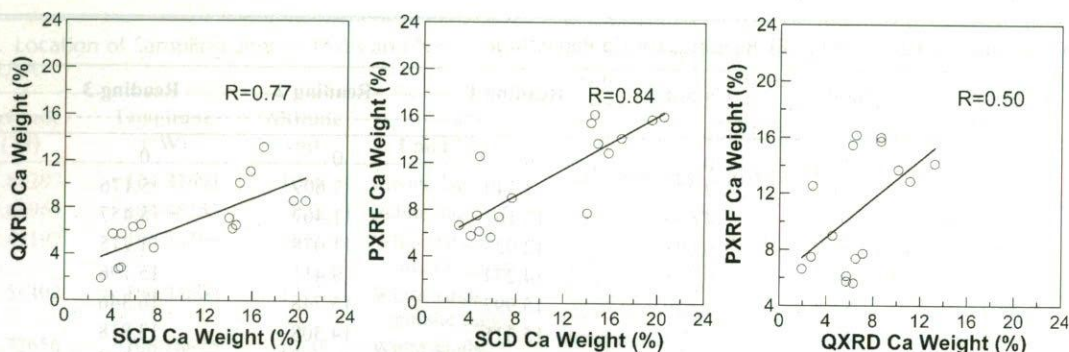


FIG. 3. Correlations of calcium (%) between QXRD and SCD (clockwise from top left), PXRF and SCD, and PXRF and QXRD.

determined by the SCD and QXRD methods and compared with SCD and QXRD gypsum.

RESULTS AND DISCUSSION

Table 3 shows the calcite, gypsum, and total Ca percentages from SCD, QXRD, and PXRF. Mean separations conducted at the $P < 0.05$ level indicated no significant differences between PXRF and SCD, and between QXRD and PXRF in Ca content. However, significant differences existed between QXRD and SCD. Correlations for Ca were best between SCD and PXRF ($R = 0.84$) (Fig. 3). For gypsum prediction by PXRF, calcite subtractions from the total Ca percentage were made with both SCD data (shown in Table 3 as PXRF Gyp-a) and QXRD data (shown in Table 3 as PXRF Gyp-b). In highly gypsic soils ($>60\%$), PXRF results were generally lower than QXRD and SCD levels. The discrepancy narrowed at lower gypsum levels. Overall, no significant differences ($P < 0.05$) were noted between SCD, QXRD, Gyp-a, and Gyp-b means. Figure 4 shows

that the best gypsum relationships were between QXRD and Gyp-b ($R = 0.96$) and QXRD and Gyp-a ($R = 0.93$).

At site 1, large differences existed in gypsum content among methods in the 0- to 4-cm horizon. The SCD (highest) and Gyp-b (lowest) gypsum percentages were 55.0% and 13.8%, respectively. The disparity in this sample is likely tied to sampling depth given the wavy boundary between the A and B₁ horizons. It is possible that the waviness of this boundary led to higher gypsum levels being sampled at a shallower depth for the SCD sample, thus inflating the percentage. Gypsum percentages of the 4- to 10-cm and 10- to 30-cm horizons were very similar between the SCD (60.0% and 61.0%) and both Gyp-a (60.4% and 66.1%) and Gyp-b (58.6% and 62.7%). However, QXRD percentages were about 25% higher (89.2% and 89.9%). Gypsum at this site was finely disseminated as a white powder, and calcite levels were very low ($<5.0\%$).

At site 2, calcite levels were substantially higher at approximately 8% to 17%. Gypsum levels were much lower than

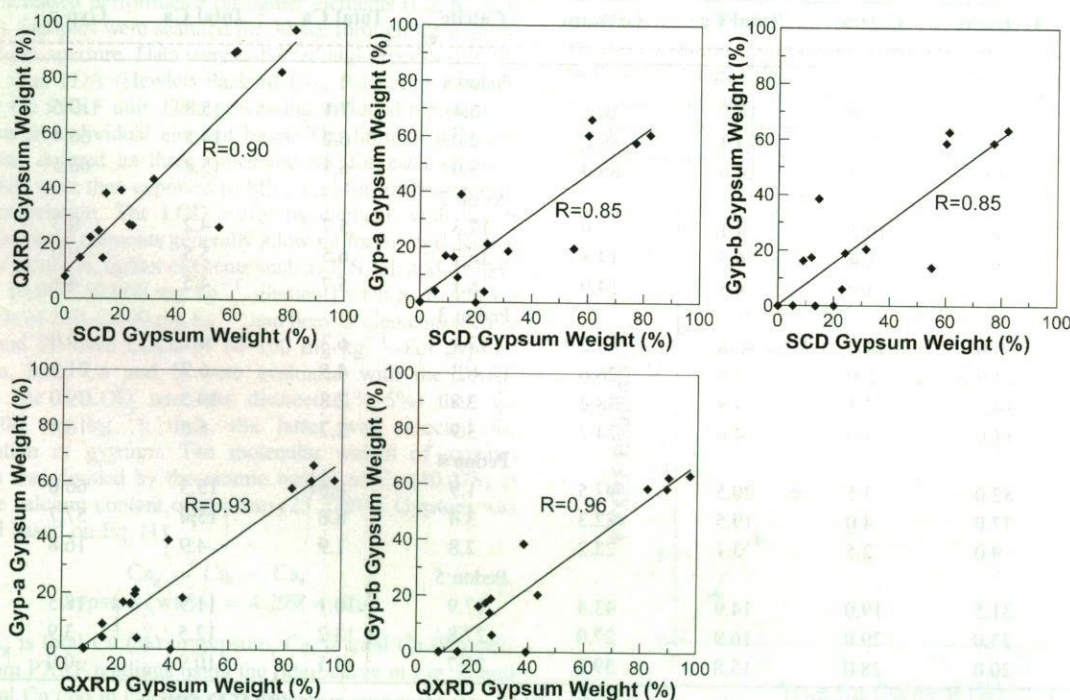


FIG. 4. Correlations of gypsum percentage between QXRD and SCD (clockwise from top left), Gyp-a and SCD, Gyp-b and SCD, Gyp-b and QXRD, and Gyp-a and QXRD.

at site 1, with both gypsum and calcite existing as isolated small masses and crystals. Gypsum levels were very low in the 0- to 6-cm horizon, with SCD and Gyp-a reporting 0% and 0.3%, respectively. Again, the QXRD gypsum percentage was higher than other methods at 7.9%. Also, calcite levels of QXRD were 7% to 8% higher than those reported in the SCD. As such, Gyp-b gypsum calculations (derived using QXRD calcite correction of total Ca) were all negative, caused by an overcorrection of calcium contributed by the QXRD calcite data. However, Gyp-a and SCD gypsum data aligned nicely (<4.5% gypsum difference for each of the three horizons).

At site 3, gypsum morphology was mostly in the form of lenticular particles 5 to 10 mm in size. Gypsum percentages for the 53- to 81-cm horizon were 24.0% (SCD), 26.6% (QXRD), 21.1% (Gyp-a), and 18.9% (Gyp-b). Similarly, gypsum percentages for the 81- to 130-cm horizon aligned nicely at 38.2% (QXRD), 39.0% (Gyp-a), and 38.5% (Gyp-b). However, gypsum differences of up to 12% among methods were noted in the 18- to 36-cm and 130- to 150-cm horizons. Given the fact that gypsum in this profile was not finely disseminated, the lenticular habit of the gypsum could have affected the fluorescence detected by the PXRF. Also, matrix masking by the gypsum-free soil could have limited the effective detection of gypsum by the PXRF. In three of four horizons at site 3, QXRD again produced the highest gypsum percentages. Calcite percentages from SCD and QXRD were very similar (<3% difference in all horizons); thus, Gyp-a and Gyp-b gypsum percentages from PXRF were very similar. Calcite was highest in the surface horizon, then decreased with depth.

Site 4 was generally low in calcite (<4.0%), but very high in gypsum in the upper part of the profile with lower levels deep in the subsoil. For the 3- to 20-cm and 58- to 89-cm horizons, PXRF gypsum content tended to be lower than QXRD and SCD data. Although considerable variation existed between PXRF, QXRD, and SCD data for each horizon, each data set showed very consistent decreasing trends with depth. All methods successfully showed a small decrease in gypsum from 3 to 20 cm to 58 to 89 cm, followed by a steep decrease in gypsum from 58 to 89 cm to 157 to 176 cm. For the three horizons considered, gypsum percentage variation among the methods decreased from 36.9% (3–20 cm) to 24.6% (58–89 cm) to 13.2% (157–176 cm) as gypsum quantity also decreased. For all three horizons, QXRD again produced the highest gypsum percentages among the methods, sometimes by more than 15%.

Site 5 displayed high levels of both calcite (17%–29%) and gypsum (>20%). Because of the substantial influence of calcite on the correction factor applied to PXRF, the QXRD and SCD gypsum data sets did not align well with the PXRF data set. However, total Ca levels aligned very well among the three data sets (<5% variability among methods). For this reason, the introduction of a scaling factor adjusting the influence of calcite on the predicted PXRF gypsum level may be appropriate. For all three horizons, QXRD again produced the highest gypsum percentages among the methods, sometimes by more than 35%.

In considering the averages of all five sites, QXRD produced the highest gypsum percentage (40.8%), followed by SCD (30.5%) and PXRF Gyp-a (24.6%) and Gyp-b (24.1%). Thus, PXRF (Gyp-a) provided results that were within 6% of SCD, the current Soil Survey Staff standard for laboratory determination of gypsum. For total Ca, SCD was highest at 10.7%, followed by PXRF (9.3%) and QXRD (6.7%). These results, along with trends observed in the data of sites 1 to 5, indicate that QXRD tends to overestimate gypsum with respect to the other methods considered.

Advantages to PXRF

The biggest advantage to using PXRF is the time saved and the opportunity to determine calcium content in the field. Literally, total Ca readings can be taken in the field in 30 sec using this technology. For conversion to gypsum percentage, field personnel must conduct a field effervescence test with HCl to identify the presence of calcite. If calcite is absent, Ca readings reported by PXRF can be directly converted to gypsum percentages. In addition, many readings can be taken across a landscape and/or within a soil profile to average out variability and obtain a more consistent gypsum estimate, whereas current use of laboratory techniques limits the scope of sampling because of costs of laboratory analyses. Finally, an inherent advantage is having the gypsum quantification performed in the field by the field staff who work in these soils and have a strong sense of expected trends, variability across the landscape, and correlations with different vegetative communities.

Disadvantages to PXRF

Several disadvantages exist with respect to using PXRF for gypsum quantification. First, the equipment is expensive. At the time this study was conducted, purchasing the equipment would cost approximately US \$30,000. Second, variability in gypsum morphology and expression can pose challenges for the PXRF. Matrix masking effects by non-gypsum-containing soil and high concentrations of calcite in the matrix could contribute to variability in readings.

Recommendations

Field personnel using this technology should standardize the PXRF and make every effort to prepare a uniform, smooth surface for scanning. For harder gypsum compounds, this might be accomplished using a small mortar and pestle, grinding the sample, and compressing it to form a smooth surface. Less than 10 g of sample should be required for these steps. Care should be taken to completely cover the PXRF orifice with sample, so all fluoresced radiation from the sample can be detected by the PXRF. Also, field personnel must determine if any calcite is present in the sample. If none is present, total Ca obtained by the PXRF can be converted directly to gypsum percentage. If calcite is present, the use of a calcimeter (pressure-sensing manometer) can be used to quantify calcite percentage. It can then be converted to total Ca and subtracted from PXRF total Ca before calculating gypsum percentage. Researchers are strongly encouraged to prepare/scan multiple samples from each horizon to address gypsum and horizon variability. Scanning time did not seem to affect total Ca readings appreciably; thus, 30 sec for each sample should be sufficient.

CONCLUSIONS

This study has shown that PXRF can produce consistent, reliable quantification of total Ca from which gypsum percentage can be determined. The use of PXRF provides results comparable (within 6%) of current Soil Survey Staff-referenced laboratory methods, but does so on-site and in a fraction of the time required for laboratory analysis. Among the three evaluated methods (PXRF, QXRD, and SCE), QXRD consistently produced the highest estimates of gypsum percentage; thought to be an overestimate based on morphological observations. Correlations for gypsum between PXRF (Gyp-b) and QXRD, and PXRF (Gyp-a) and QXRD, produced *R* values of 0.96 and 0.93, respectively. However, correlations for calcium were highest between PXRF and SCD (*R* = 0.84). In 87% of evaluated samples, moisture content and grinding of samples did not significantly affect PXRF

readings. Use of the PXRF requires careful consideration of variables such as matrix-masking effects, calcite present, gypsum particle morphology, and so on. Careful preparation of samples, however, can overcome most of these obstacles and provide for reliable, accurate results.

REFERENCES

- Busacca, A. J., and M. J. Singer. 1989. Pedogenesis of a chronosequence in the Sacramento Valley, California, USA, II. Elemental chemistry of silt fractions. *Geoderma* 44:43–75.
- Celis, B. 1996. X-ray fluorescence analysis of gold ore. *J. Appl. Spectrosc.* 50(5):572–575.
- Eberl, D. D. 2003. User's guide to RockJock—a program for determining quantitative mineralogy from powder X-ray diffraction data. U. S. Geol. Surv. Open file report 03–78.
- Ge, L., W. Lai, Y. Lin, and S. Zhou. 2005. In situ application of FPXRF techniques in mineral exploration. In *IAEA-TECDOC-1456 In Situ Applications of X ray Fluorescence Techniques*. International Atomic Energy Agency, Vienna, Austria, p. 61–108.
- Gee, G. W., and J. W. Bauder. 1986. Particle size analysis. In A. Klute (ed.) *Methods of Soil Analysis Part 1: Physical and Mineralogical Methods*. 2nd ed. ASA-SSSA, Madison, WI.
- International Union of Soil Science. 2006. World Reference Base for Soil Resources. Food and Agriculture Organization of the United Nations, Rome, Italy.
- Jones, R. C., W. H. Hudnall, and W. S. Sakai. 1982. Some highly weathered soils of Puerto Rico, 2. Mineralogy. *Geoderma* 27:75–137.
- Kalnicky, D. J., and R. Singhvi. 2001. Field portable XRF analysis of environmental samples. *J. Hazard. Mater.* 83:93–122.
- Schulin, R., F. Curchod, M. Mondeshka, A. Kaskalova, and A. Keller. 2007. Heavy metal contamination along a soil transect in the vicinity of the iron smelter of Kremikovtzi (Bulgaria). *Geoderma* 140:52–61.
- Sherrod, L. A., G. Dunn, G. A. Peterson, and R. L. Kolberg. 2002. Inorganic carbon analysis by modified pressure-calciometer method. *Soil Sci. Soc. Am. J.* 66:299–305.
- Soil Survey Staff. 1999. *Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys*. 2nd ed. US Government Printing Office, Washington, DC.
- Soil Survey Staff. 2004. *Soil Survey Laboratory Methods Manual*. Version 4.0. Soil Survey Investigations Report No. 42. US Government Printing Office, Washington, DC.
- Soil Survey Staff. 2008. Soil characterization data for pedons in Otero County, New Mexico [online]. Available at <http://ssldata.nrcs.usda.gov/> (verified 19 May 2008).
- US Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. In *Agriculture Handbook* 60. U.S. Gov. Print. Office, Washington, DC.
- Weindorf, D. C., R. Sarkar, M. Dia, H. Wang, Q. Chang, B. Haggard, A. McWhirt, and A. Wooten. 2008. Correlation of X-ray fluorescence spectrometry and inductively coupled plasma atomic emission spectroscopy for elemental determination in composted products. *Compost Sci. Util.* 16(2):79–82.
- Zhu, Y., and D. C. Weindorf. 2009. Determination of soil calcium using field portable XRF. *Soil Sci.* 174(3):151–155.